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㉔ **New polymer-modified, oxidized asphalt compositions and methods of preparation.**

㉕ Disclosed in this invention are novel asphaltic compositions having improved viscoelastic properties and storage stability. They contain neutralized mixtures of oxidized asphalt and an acid functionalized polymer, which polymer is selected from the group consisting of sulfonated EPDM, sulfonated styrene-butadiene, and acrylic acid terpolymers, in an amount that is sufficient to result in an asphaltic composition having a softening point greater about 55°C and a viscosity in the range from about 150 cP to 2000 cP or from about 3000 cP to about 8000 cP at 135°C. The basic neutralizing agent used in these compositions contain cations having a valence of from +1 to +3, preferably +2. The invention also relates to the products produced by the process and method of making the compositions. The compositions can be used as a binder in paving applications, particularly as a binder in dense graded and in open graded hot mix pavements.

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The present invention relates to asphaltic compositions having viscoelastic properties that are suitable for use as binders in dense graded and open graded hot mix asphalt pavement. The compositions comprise blends of asphalt or bitumen and synthetic polymers which are stable in storage between the time of preparation and the time of use in hot mix pavement. The present invention also relates to methods of preparing and methods 5 of using the compositions and the products produced by the process of the present invention. The terms asphalt and bitumen are used interchangeably herein.

Asphalt is a bituminous arterial remaining after, or prepared from, the distillation of crude oil. Typically, asphalt is derived from the bottoms of a vacuum distillation tower and has an atmospheric equivalent boiling point of generally at least 350°C. Because it is hydrophobic and has good adhesiveness and weatherability, 10 asphalt can be used as an adhesive or binder component of road paving materials. When so used, asphalt is normally mixed with aggregate (i.e., rock), typically in a ratio of about 5 wt.% asphalt to 95 wt.% aggregate.

Asphalt, however, has certain physical properties that vary widely with changes in temperature. For this 15 reason, polymers often are added to asphalt to extend the range of its physical properties. Polymers can reduce the tendency of the asphalt to creep and rut in warm weather by increasing its high temperature viscoelastic stiffness; typical paving grade asphalts have softening points below 50°C, while softening points greater than 55°C are desired for resistance to creep in hot weather; and polymers can minimize cracking and stripping in cold weather by improving the asphalt's low temperature viscoelastic properties.

However, not all asphalts and polymers form compatible mixtures having storage stability. "Storage 20 stability" is defined as the formation of a continuous phase or two continuous phases that do not separate on standing for a specified period of time, usually 3-5 days, at a specified temperature, usually 160°C. The storage stability of polymer modified asphalt is greatly affected by the compatibility of the asphalt with the particular 25 polymer. Incompatible and partially compatible mixtures easily undergo phase separation.

Furthermore, some polymer modified asphalts are suitable for roofing applications but cannot be used in 25 hot mix paving applications where the blend must be sufficiently fluid at mixing temperature to adequately coat the aggregate particles. For example, an asphalt binder for dense graded hot mix paving should have a viscosity at 135°C between 150 and 2000 cP, and a binder for open graded hot mix should have a viscosity at 135°C between 3000 and 8000 cP.

Various methods have been suggested for making polymer-modified asphalt compositions that are sufficiently compatible to be acceptably storage stable and that also have viscosities and softening points in the 30 range required for a particular type of application. Some, for example, rely on selection of the appropriate polymer and other additives and require a specific sequence of blending and reaction steps to effect the final properties of the asphalt-polymer mixture (see, for example, U.S. Patent No. 4,600,635 for use of a bitumen-based adhesive composition comprising bitumen, oil, and an ionomeric elastomer (such as sulfonated, carboxylated or phosphonated EPDM or butyl rubber) in less than 15% weight, preferably 3%-8%, that is neutralized by metal 35 cations; British Patent No. 1,534,183 discloses *inter alia* use of a metal alcoholate and the addition of from 5% to 95% wt. of an ethylene/vinyl ester copolymer and bitumen partially crosslinked by means of -O-M-O-, -O-B-O- or -O-CRR'-O-bridges; or U.S. 4,882,373 for acid modification of asphalt with subsequent contact with an oxygen-containing gas, and mixing with a thermoplastic elastomer, and an unsaturated functional monomer.)

40 European Patent No. 38,721 (U.S. Patent No. 4,371,641) teaches that a polymer, preferably an unsaturated elastomer, e.g., EPDM or butyl rubber, or a thermoplastic polymer (from 5-25 wt.%) and an appropriate filler can be added to airblown asphalt to make it suitable for use as a roofing material by increasing the asphalt's stability towards oxidation and decreasing its sensitivity to ultraviolet radiation. The thermoplastic or elastomeric polymer must contain anionic groups such as carboxylate, phosphonate or, preferably, sulfonate groups 45 which can be neutralized by addition of a salt of a carboxylic acid, preferably a metal acetate, more preferably zinc acetate. Applicants have found that the weight percents of polymer specified in this disclosure produce blends that are too viscous to coat the aggregate in hot mix paving materials.

Accordingly, none of the foregoing references teaches nor suggests the asphaltic compositions having the storage stability and viscoelastic properties over a wide range of temperatures required to produce a superior 50 binder for dense graded and open graded hot mix asphalt for road paving applications that is disclosed by the applicants, nor do they teach nor suggest the process of preparing or using applicants' composition.

This invention relates to asphaltic compositions that are storage stable and have viscoelastic properties 55 over a wide range of temperatures that make them suitable for use as superior binders for dense graded and open graded hot mix asphalt for road paving applications. The compositions comprise neutral mixtures of oxidized asphalt and acid functionalized polymer, the mixtures having softening points greater than 55°C and viscosities measured at 135°C in a range from about 150 to about 2000 cP for dense graded pavement or from about 3000 to 8000 cP for open graded pavement, wherein the polymer is selected from the group consisting of sulfonated EPDM, sulfonated styrene butadiene, and acrylic acid terpolymers, and wherein the polymer is

preferably present in an amount by weight percent of total composition; that is:

- (a) more than zero but less than about 4 wt.%, preferably from about 2 to about 3 wt.% of total composition for sulfonated EPDM, or
- (b) from about 2 to about 7 wt.% of total composition for acrylic acid terpolymers or sulfonated styrene butadiene

and wherein the neutral mixture contains cations of a basic neutralizing agent having a valence from +1 to +3, specifically +1, +2 and +3. More particularly, the neutralizing agent may be selected from the group consisting of amines, ammonia, and bases that contain cations selected from the group consisting of Groups IA, IIA, IIIA and Group B elements and mixtures thereof. The term "EPDM" is used as defined in ASTM D-1418; "acrylic acid terpolymers" means terpolymers of ethylene, vinyl acetates or alkyl acrylates and from 1 to 6% acrylic acid as a co-monomer having a melt index of about 1 to about 5; and "sulfonated styrene-butadiene" means sulfonated styrene-butadiene linear diblock and sulfonated styrene-butadiene-styrene linear and radial triblock copolymers, which copolymers are not hydrogenated. This invention also relates to a method for making and using the compositions, and includes the products produced by the process disclosed herein. More specifically, the asphaltic compositions have improved phase compatibility between a neutral blend of oxidized asphalt and acid functionalized polymer and are storage stable. Oxidation is accomplished by means of airblowing.

In order to be suitable as a binder in open graded or dense graded pavement, a polymer-modified asphalt must have certain characteristics. It must be liquid-like on application, but harden on cooling, be able to resist rutting, cracking and stripping and should be storage stable as a hot fluid. In order to achieve the necessary liquid-like properties, the polymer-modified asphalt must have a lower range of viscosities and softening points than is needed in certain other applications such as roofing materials. Viscosities in the range of from about 150 to 2000 cP at 135°C for dense graded, and from about 3000 to 8000 cP at 135°C for open graded pavement binders are required in the compositions of the present invention. Softening points in the range of greater than about 55°C to about 65°C as a binder for dense graded and from about 60°C to about 75°C as a binder for open graded pavement are preferred. While addition of polymers can impart the needed viscoelastic properties to the material, the type of polymer and the manner in which the asphalt and polymer are modified also can influence the compatibility and storage stability of the resulting asphaltic composition. It is economically very desirable that the asphaltic composition be storage stable if it is to be used as a binder in road paving materials.

One embodiment of the present invention, described below, is processes for making the novel asphaltic compositions. Another embodiment is the compositions themselves, including the products produced by the processes described herein.

Thus, the compositions of the present invention exhibit improved viscoelastic properties and storage stability are produced by combining an oxidized asphalt, an acid functionalized polymer wherein the polymer is selected from the group consisting of sulfonated EPDM, sulfonated styrene butadiene, and acrylic acid terpolymers, and wherein the polymer is preferably present in an amount by weight percent of total composition less than or equal to about 7 wt.% that corresponds to an amount sufficient to result in an asphaltic composition having a viscosity within the foregoing range, and a basic neutralizing agent, and wherein if the polymer is sulfonated EPDM the weight percent of polymer is required to be greater than zero and less than about 4 wt.%, and preferably 2-3 wt.%, and wherein if the polymer is selected from the group consisting of sulfonated styrene butadiene and acrylic acid terpolymers the weight percent of polymer is required to be from about 2 wt.% to about 7 wt.%, preferably from about 3 wt.% to about 5 wt%. When the polymer is acrylic acid terpolymer, the polymer contains ethylene and acrylic acid monomers and co-monomers selected from the group consisting of vinyl acetates, alkyl acrylates and/or mixtures thereof. In the case of sulfonated polymers, sulfonation should be accomplished prior to combining with the oxidized asphalt and should be at a level of less than about 15 mole percent, and may be performed by any means known to one skilled in the art. For example, sulfonation may be accomplished using acetyl sulfate or, more preferably, sulfuric acid. Thereafter the sulfonated polymers are neutralized.

The asphalts used in the present invention may be obtained from a variety of petroleum residua and may be classified by their penetration (measured according to Standard Specification ASTM D-5). Typically, the asphalt will have a nominal atmospheric boiling point at least 350°C and more typically above 440°C. In the process of the present invention, the asphalt is oxidized by airblowing in any manner known to one skilled in the art. Oxidation is carried out at a temperature ranging from about 180°C to 300°C; more preferably, from about 200°C to about 250°C for about 3 hours to about 12 hours for commercial processes. Generally, the procedure followed is to oxidize the asphalt to a pre-selected softening point, usually greater than 100°C, and a relatively high viscosity, then blend in flux, which may be the original asphalt or other asphaltic material, to decrease the viscosity into the target range desired. Selection of the desired final viscosity is generally based on experience and is within the skill of a routineer in the art, given the ranges disclosed in the present invention. The term "oxidized asphalt" in this disclosure and in the claims of this invention means any blend of oxidized

and unoxidized asphalts so prepared.

In the process of making the novel asphaltic compositions, the oxidized asphalt and acid functionalized polymer mixture may be combined using any number of methods known to one skilled in the art. These may include dissolution with stirring in a suitable solvent such as dichloroethane for the asphalt and toluene for the polymer, or heating the oxidized asphalt to about 140°C to 170°C and thereafter adding the polymer *in situ* in portions with stirring or agitation, the latter preferably using a high shear mixing device. The method used will influence the amount of time needed to combine the oxidized asphalt and polymer, but in any event should be sufficient to distribute the polymer throughout the asphalt. Times may range from 1/2 to 24 hours, according to the method used.

The basic neutralizing agent contains cations having a valence from +1 to +3 specifically +1, +2 and +3, and may be selected from the group consisting of ammonia, amines, bases that contain cations selected from the group consisting of Groups IA, IIA, IIIA, and Group B of the Periodic Table and mixtures thereof. The preferred basic neutralizing agent is one that contains one or more monovalent or divalent cations, preferably divalent cations. These may preferably be Zn⁺², Ca⁺², Ba⁺², Mg⁺² and mixtures thereof, or more preferably Zn⁺² and Ca⁺². Suitable compounds containing such cations are, for example, zinc acetate, zinc oxide or calcium oxide, more preferably calcium oxide. The basic neutralizing agent may be contained in a suitable solvent, such as water/methanol before adding to the oxidized asphalt-polymer mixture, or may be added *in situ*, for example, in powdered or other undissolved form. The order of neutralization is not important. Thus, for example, the polymer may be neutralized and then combined with the oxidized asphalt or the oxidized asphalt and acid functionalized polymer may be combined and then neutralized. Preferred for acrylic acid terpolymers is the addition of basic neutralizing agent *in situ* directly to the heated oxidized asphalt or to oxidized asphalt-acid functionalized polymer mixture. It is necessary that sufficient neutralizing agent be added to neutralize the oxidized asphalt and acid groups on the polymer. Generally this will require a stoichiometric amount or, preferably a slight excess of neutralizing agent.

It is possible to adjust the softening point and viscosity of the asphaltic composition by varying the amount of oxidized asphalt and polymer in the composition. However, it is a requirement of the present invention that the resulting asphalt-polymer compositions have a viscosity in the range from about 150 to about 2000 cP for binders for dense graded pavement and from about 3000 to about 8000 cP for binders for open graded asphalt pavement, measured at 135°C. Hence, the weight percent of polymer in comparison to the weight percent of the total composition must be adjusted accordingly. At all times the amount of polymer will be less than 7 wt.%. However, in the case of sulfonated EPDM the weight percent of polymer in the composition is required to be greater than zero to less than about 4 wt.%, preferably from about 2 to about 3 wt.%; in the case of sulfonated styrene butadiene and acrylic acid terpolymers the weight percent is required to be from about 2 to about 7 wt.%, preferably from about 3 wt.% to about 5 wt.%. It is at these amounts that the asphaltic compositions possess the necessary viscoelastic character to enable their use as a binder in open graded and dense graded road paving materials, while showing the storage stability characteristic of the materials of this invention.

It has been found that, compared with untreated asphalt or functionalized airblown asphalt alone, the compositions of the present invention form compatible blends which remain storage stable after holding for 4 days at 160°C, have improved viscoelastic properties and softening points and have viscosities that are within the targets required for the particular binders.

In the present invention, softening point was used as a measure of compatibility and storage stability. If the top third and bottom third of each sample stored at 160°C for 4 days showed softening points within about a 4°C variation, the asphalt and polymer were judged compatible. However, in order to supplement the softening point data optical micrographs were taken of the top and bottom segments of the asphaltic compositions to verify phase compatibility.

The invention is illustrated by reference to the following examples, which are not intended to limit the scope of the invention.

Example 1

Oxidation was accomplished by heating the asphalt (asphalt is a Billings asphalt of penetration grade 120/150) to 200°C with stirring for 2 hours and by passing air through the asphalt with an inlet at the bottom of the flask. The effect of airblowing on softening points and viscosities is shown in the table below (Samples (B) through (G)). After the 2 hour oxidation period, the asphalt (360.2g) was cooled to 150-160°C, and 7.2g of polymer (an ethylene methyl acrylate-acrylic acid terpolymer, containing 1% acrylic acid and 23% methyl acrylate, melt index equal to 5) was added with stirring and the stirring continued for about 1 hour. The neutralizing agent (3.85g of zinc oxide) was added and the mixture stirred an additional hour. The data below indicate that the polymer-asphalt blends' softening points and viscosities are improved over the starting asphalt,

and that storage stability is achieved for the oxidized asphalt-terpolymer blend only when neutralizing agents are added.

In microscopic examination of the top one third ("T") and bottom one third ("B") portion of each sample, it was found that Samples D and E contained similar amounts of polymer. Samples C and F had significantly more polymer in the top phase than in the bottom. Sample (G) showed slightly more polymer in top than in the bottom sample but still remained within the range of compatible blends.

TABLE

Sample	Polymer (wt%)	Neutralizing Agent	Initial Softening Point ⁽¹⁾ °F (°C)		Viscosity ⁽²⁾ cP, 135°C	Softening Point, °F ⁽¹⁾ Top Bottom	
			°F	°C		Top	Bottom
(A)	0	None	107	(42)	257	*	*
(B)	0	None	117	(47)	450	*	*
(C)	2	None	125	(52)	654	132	126
(D)	2	ZnO	127	(53)	673	130	129
(E)	2	CaO	128	(53)	720	132	132
(F)	4	None	131	(55)	1060	137	131
(G)	4	CaO	135	(57)	1262	138	135

Legend

The viscosity for the asphalt-polymer compositions of the present invention must fall within the target range of from about 150 cP to 2000 cP and from about 3000 cP to about 8000 cP at 135°C. Samples (D), (E), and (G) formed compatible blends, based on softening point data and optical microscopy. Blends (C) and (F) were shown to be phase-separated by optical microscopy.

(A) Starting asphalt unoxidized
(B) through (G) Oxidized Sample (A)

(1) ASTM D36 standard test method for softening point of asphalt ring-and-ball apparatus.

(2) ASTM D4402 standard test method for viscosity of unfilled asphalts using the Brookfield thermosel apparatus.

* Not measured

Example 2

An unoxidized asphalt (Baytown AC-10) was blended with a commercially prepared airblown coating grade of asphalt ("coating grade" as used herein means highly oxidized asphalt having a softening point of at least 205°F (96°C)). Coating grade was prepared from Tia Juana Medium residuum. In this example, Zn-sulfonated EPDM was used to compare an air oxidized asphalt prepared as in Example 1, with an asphalt prepared by blending an unoxidized asphalt (Sample A) with an airblown coating grade. In this example, 20 wt.% of the coating grade material was blended at 160°C with 80 wt.% of unoxidized asphalt.

TABLE

5	Sample	Polymer (wt%)	Neutralizing Agent	Initial Softening Pt		Viscosity cP, 135°C	Softening Point °F Top Bottom	
				°F (°C)	°F (°C)		Top	Bottom
10	(A)	0	None	107	(42)	278	*	*
	(B)	0	None	122	(50)	514	*	*
	(C)	1	CaO	129	(54)	918	127	128
	(D)	0	None	116	(47)	421	*	*
	(E)	1	CaO	123	(51)	1034	128	133

Legend

The target range of viscosity is from about 150 to 2000 cP and from about 3000 to about 8000 cP (for dense graded and open graded binder, respectively) for asphaltic compositions of the present inventions. Samples (C) and (E) formed compatible blends, as confirmed by optical microscopy.

* Not measured

- (A) Starting asphalt
- (B) Oxidized Sample (A)
- (C) Oxidized Sample (A)
- (D) 80% Sample (A) + 20% coating grade asphalt
- (E) 80% Sample (A) + 20% coating grade asphalt

30 Softening points and viscosities were measured as in Example 1.

Example 3

35 A Zn-sulfonated EPDM (the polymer was separately neutralized) was mixed with a coating grade asphalt at 160°C (320°F). Properties of this blend (Sample C) are shown in the table below and are seen to be too high in softening point and viscosity to be useful in asphalt binder applications. Coating grade was prepared from Tia Juana Medium residuum. Unoxidized asphalt (Baytown AC-5) was blended back to the coating grade-polymer blend to adjust the properties into the target range. Data in the table below indicate that this is effective. All blending was done at 160°C (320°F) although temperatures below that can be used in providing the blends are low enough in viscosity to allow good mixing.

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TABLE

5	<u>Sample</u>	<u>Polymer (wt%)</u>	<u>Initial Softening Pt °F (°C)</u>	<u>Viscosity cP, 135°C</u>
	(A)	0	102 (39)	260 (approx.)
	(B)	0	205 (96)	14000
10	(C)	4	263 (128)	24425
	(D)	3.2(a)	232 (111)	4250 (at 350°F; 177°C)
	(E)	2(a)	169 (76)	5125
	(F)	1.5(a)	154 (68)	3260

Legend

15 The target range of viscosities for asphaltic compositions of the present invention is from about 150 to 2000 cP and from about 3000 to about 8000 cP for dense graded and open graded binder, respectively, measured at 135°C. Samples D, E, & F were all storage stable.

20 (A) Starting asphalt
 (B) Coating grade asphalt
 (C) Coating grade asphalt + polymer
 25 (D) 20% starting asphalt + 80% coating grade asphalt-polymer blend produced in (C)
 (E) 50% starting asphalt + 50% coating grade asphalt-polymer blend produced in (C)
 30 (F) 63% starting asphalt + 37% coating grade-polymer blend produced in (C)

Softening points and viscosities were measured as in Example 1. (a) Calculated

Example 4

35 A feedstock was prepared by blending 20 wt. % of an airblown coating grade asphalt (softening point 195°F; viscosity 12,580 cP at 275°F (135°C) with 80% of an unoxidized asphalt (AC-3) (softening point 61°F (16°C); viscosity 70 cP at 275°F (135°C). Coating grade was prepared from Tia Juana Medium residuum. Unoxidized 40 asphalt was prepared from a blend of naphthenic crude oil residua. The resulting 80/20 blend had a softening point of 117°F (47°C) and a viscosity of 388 cP at 275°F (135°C). To 376.8g of this 80/20 blend, heated at 320°F (160°C), 11.3g of a sulfonated zinc neutralized styrenebutadiene-styrene triblock radial copolymer was added, and the mixture was stirred for 2 hours. The resulting polymer-asphalt blend had a softening point of 153°F (67°C) and a viscosity of 1042 cP at 275°F (135°C). It was storage stable after 4 days at 160°C, having a bottom 45 and top softening point of 164°F (73°C) and 165°F (74°C), respectively. The storage stability was also confirmed by optical microscopy. In another vessel, 338g of the 80/20 blend was heated to 320°F (160°C) and 10.15g of a sulfonated zinc neutralized styrene-butadiene diblock copolymer was added, and the mixture stirred for 2 hours. The resulting polymer modified asphalt had a softening point of 135°F (57°C) and a viscosity 50 of 1074 cP at 275°F (135°C). It was storage stable after 4 days at 160°C (both top and bottom samples had softening points of 140°F (60°C), and the storage stability was confirmed by optical microscopy. Other blends were made with the same 80/20 asphalt feed and the same amounts of unsulfonated polymers. These blends were not storage stable, having bottom and top softening points of 130° and 212°F, respectively, for the SBS blend and 141° and 129°F, respectively, for the SB blend.

55 Similar experiments were carried out using an air oxidized Baytown AC-10 asphalt prepared as described in Example 1. Data are shown in the table below. Softening points and viscosities were measured as in Example 1.

TABLE

Sample	Polymer	Softening Pt. °F (°C)	Viscosity 135°C	Softening Bot- tom	Pt. °F Top
(Ac-10) Bitumen	None	107 (42)	278	-	-
Air Oxidized	None	127 (53)	638	-	-
Air Oxidized	2% Zn Sulfo- SBS	128 (53)	832	126	127
Air Oxidized	2% Zn Sulfo-SB	144 (62)	1806	142	142
Air Oxidized	4% Zn Sulfo-SB	153 (67)	3610	154	154

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Example 5

Another blend of 20% coating grade and 80% of unoxidized Tia Juana Medium asphalt was prepared. Coating grade was prepared from Tia Juana Medium residuum. It had a softening point and viscosity as shown in the table below. 3 wt.% of a zinc neutralized sulfonated SBS radial triblock copolymer was added to this blend. In another blend 3 wt.% of the unsulfonated SBS was added. Data below indicate the necessity of having a sulfonated SBS radial triblock copolymer. Softening points and viscosities were measured as in Example 1.

TABLE

Polymer	Initial Softening Pt. °F (°C)	Viscosity 135°C	Softening Bottom	Pt. °F Top
None	115	408		
3% SBS	140 (60)	2465	135	210
3% ZnSulfo SBS	158 (70)	3355	163	165

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Claims

1. An asphaltic composition having improved storage stability, which comprises a storage stable mixture of an oxidized asphalt, a sulfonated polymer selected from sulfonated EPDM, sulfonated styrene-butadiene linear diblock, sulfonated styrene-butadiene-styrene linear triblock and sulfonated styrene-butadiene-styrene radial triblock copolymers, and acrylic acid terpolymers, and a basic neutralizing agent, wherein the polymer is present in an amount that is sufficient to result in a storage stable composition having a softening point greater than about 55°C and a viscosity in the range of from about 150 cPs to about 2000 cPs or from about 3000 cPs to about 8000 cPs measured at 135°C.
2. The composition of claim 1 wherein the polymer is sulfonated EPDM and wherein the polymer is present in an amount of more than zero and less than about 4 wt.% total composition.
3. The composition of claim 1 wherein the polymer is sulfonated EPDM in an amount from about 2 wt.% to about 3 wt.% total composition.
4. The composition of claim 1 wherein the polymer is selected from sulfonated styrene-butadiene linear diblock, styrene-butadiene-styrene linear and styrene-butadiene-styrene radial triblock copolymers in an amount from about 2 wt.% to about 7 wt.% total composition.
5. The composition of claim 1 wherein the polymer is selected from sulfonated styrene-butadiene linear diblock, styrene-butadiene-styrene linear and styrene-butadiene-styrene radial copolymers in an amount from about 3 wt.% to about 5 wt.% total composition.

6. The composition of claim 1 wherein the polymer is an acrylic acid terpolymer in an amount of from about 2 wt.% to about 7 wt.% total composition.
7. The composition of any preceding claim wherein the basic neutralizing agent contains cations having a valence of from +1 to +3.
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8. The composition of claim 7 wherein the basic neutralizing agent contains cations selected from Ca^{+2} , Zn^{+2} , Ba^{+2} , Mg^{+2} , and mixtures thereof.
9. The method of preparing the composition of any preceding claim wherein oxidized asphalt, acid functionalized polymer and basic neutralizing agent are combined in situ at a temperature from above about 10 140°C to about 250°C.
10. The method of preparing the composition of any of claims 1 to 8 wherein the acid functionalized polymer is first neutralized, and then combined with the oxidized asphalt at a temperature from above about 140°C to about 250°C.
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 441 285 (THE DOW CHEMICAL COMPANY) 14 August 1991 * page 2, column 2, line 15 - line 18 * * page 3, column 3, line 7 - column 4, line 20 * * page 3, column 4, line 28 - line 31 * * page 4, column 6, line 14 - line 19 * * examples 1,2 * ---	1-5,10	C08L95/00
D,A	US-A-4 371 641 (G.A.M. BOYER; I. DUVDEVANI; J-M. A. MULLER) 1 February 1983 * the whole document *	1-10	
A	WO-A-8 606 736 (SOCIÉTÉ FRANÇAISE DE PETROLES BP; THE BRITISH PETROLEUM COMPANY) 20 November 1986 * example 1 *	1-10	
A	DATABASE WPI Week 7513, Derwent Publications Ltd., London, GB; AN 75-22059W & SU-A-429 079 (LENINGRAD LENSOVET TECH) 24 October 1974 * abstract *	1-10	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C08L
A	US-A-4 544 690 (D.J. LADISH) 1 October 1985 * column 2, line 38 - line 50 * * column 3, line 15 - line 20 * * column 5, line 59 - line 66 * * example 1 *	1-10	

The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 28 JUNE 1993	Examiner GOERKE H.R.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

PCT/FR00/01711, filed June 21, 2000
REQUEST FOR EARLY NOTIFICATION OF SERIAL NUMBER

Inventor(s): Jean-Pascal PLANCHE, Patrick TURELLO, Pierre
CHAVEROT, Patrice VEGNY.

Title: METHOD FOR THE PRODUCTION OF CROSS-LINKED
AND/OR FUNCTIONALIZED BITUMEN/POLYMER
COMPOSITIONS AND USE OF SAID COMPOSITIONS IN
COVERINGS

JC10 Rec'd PCT/PTO 21 DEC 2001
Atty Doc. #: Q67797 Client: CABINET JOLLY

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